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(54) Title: DC CAST AL ALLOY

(57) Abstract: There is disclosed a DC cast alloy of composition (in wt%): Fe 0.8-1.5 Si 0.7-0.95 Mn 0.2-0.5 Zn 0.2-0.8 Mg up to 0.2 Cu up to 0.2 Ti <0.1 B <0.01 C <0.01 Unavoidable impurities up to 0.05 each, 0.15 total Al balance. Also disclosed is a method of DC casting the alloy to form an ingot.



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### DC CAST Al ALLOY

This invention relates to an aluminium alloy, particularly one which has been DC cast and is used for finstock in heat exchangers.

The automotive heat exchanger market requires finstock alloys that offer, at low cost, a balance of physical and chemical properties, i.e. strength, formability, sag resistance, corrosion resistance, thermal conductivity and brazeability.

Aluminium alloy heat exchangers, provided with header plates, tank units, tubes for coolant (water based) and fins for improved heat exchange, are very widely used in the automobile industry and elsewhere. Generally the fins are joined to the tubes by brazing. In order to reduce corrosion of the tubes with consequent leakage of coolant, it has been common practice to make the fins electronegative relative to the tubes so that the fins act as sacrificial anodes. This has been achieved by adding Zn, Sn or In to the metal used to form the fins.

Nevertheless, there is a need to balance the sacrificial effect with the need to maintain thermal performance throughout the service life of the heat exchanger. If fins corrode too rapidly, the heat transfer characteristics are severely compromised. Additionally, use of a higher strength fin material in a particular construction can offer the opportunity to downgauge the fin and/or the tube material to achieve lower weight targets. The use of continuously cast materials can, because of the very high solidification rates ( $>10^{\circ}\text{C}/\text{sec}$ ), be utilised to achieve the higher conductivity levels required when downgauging.

WO-A-00/05426 discloses a high conductivity aluminium fin alloy. The invention disclosed therein relates to continuous strip casting of an Al alloy, where the finstock has a conductivity after brazing of greater than 49.0% IACS. During continuous casting a thin strip is produced which cools quickly.

Al-Fe-Si alloys are disclosed in, for example, the following documents: GB 1524355, GB 1524354, WO-A-00/05426, JP-A-2000169926, JP-A-080218143, JP-A-060145861, JP-A-040154931, JP-A-010195257. The

compositions of the alloys exemplified in these documents varies, but there is no disclosure of DC cast alloys.

According to a first aspect of the present invention, there is provided a DC cast alloy of composition (in wt%):

Fe	0.8 - 1.5
Si	0.7 - 0.95
Mn	0.2 - 0.5
Zn	0.2 - 0.8
Mg	up to 0.2
Cu	up to 0.2
Ti	<0.1
B	<0.01
C	<0.01

Unavoidable impurities up to 0.05 each, 0.15 total

Al balance.

The alloy could, for example, be used in header plate, or side support applications, and may have other uses, but it is primarily intended as a finstock alloy for heat exchangers.

Preferably, Cu is present in the range 0.05 - 0.2, even more preferably 0.1 - 0.15. When present, Cu is included as a solid solution strengthening component.

Mg is preferably present as a strengthening component. At high concentrations, an undesired MgO deposit is formed on the metal surface during brazing. The Mg concentration is controlled at levels where this is not a problem. Higher levels of Mg will, in the presence of  $K_3AlF_6$  and  $KAlF_4$  flux mixtures, lead to the formation of high melting point aluminium fluorides which have a deleterious effect on clad fluidity. Preferably, Mg is present in the range 0.05 - 0.2, even more preferably 0.1 - 0.15.

The strengthening effect of the Cu and Mg has to be balanced against the reduction of thermal conductivity caused by these elements.

Fe is preferably present in the range 0.8 – 1.4, although an even more preferred upper limit of the range is 1.35. Higher levels cause the formation of excessively large intermetallic particles.

Si above the upper limit of 0.95% reduces the solidus of the alloy to below 610°C which is unacceptable as it is too close to the brazing temperature. The lower limit is determined by the amount of Si necessary to achieve the required post braze strength.

Mn if present in amounts more than 0.5% has a deleterious effect on the thermal conductivity. Below 0.2%Mn there is insufficient strengthening effect.

Zn is added to make the finstock more electro-negative than, and sacrificial to, the tube material of the heat exchanger. Above 0.8%Zn, the fin becomes too electro-negative. Such high levels of Zn are detrimental to the thermal conductivity of the fin. Below 0.2%Zn, the fin is not sufficiently electro-negative to be sacrificial. The preferred range is 0.5 to 0.7%Zn.

According to a second aspect of the present invention, there is provided a DC cast aluminium alloy finstock having a composition (in wt%):

Fe	0.8 - 1.5
Si	0.7 – 0.95
Mn	0.2 – 0.5
Zn	0.2 - 0.8
Mg	up to 0.2
Cu	up to 0.2
Ti	<0.1
B	<0.01
C	<0.01

Unavoidable impurities up to 0.05 each, 0.15 total

Al balance.

The finstock sheet may be clad with a layer of aluminium alloy that is rich in silicon. Suitable alloys are AA4343 and AA4045 although other silicon rich alloys may be used. The silicon rich layer may optionally contain additions such as Zn or Sn or In that render the fin more electronegative.

This finstock may have the above-mentioned preferable or optional features. Preferably the finstock has a conductivity after brazing of at least 45% IACS.

The aluminium alloys of this invention are DC cast, and the reasons for this are described in further detail below.

There is also provided a brazed heat exchanger having fins of the above-mentioned alloy.

According to a further aspect of the present invention, there is provided a method of producing an ingot from an alloy of composition (in wt%):

Fe	0.8 - 1.5
Si	0.7 - 0.95
Mn	0.2 - 0.5
Zn	0.2 - 0.8
Mg	up to 0.2
Cu	up to 0.2
Ti	<0.1
B	<0.01
C	<0.01

Unavoidable impurities up to 0.05 each, 0.15 total

Al balance,

which method comprises DC casting the alloy to form an ingot.

In this aspect, the present invention is therefore aimed at producing the ingot by conventional DC casting, thereby avoiding the need for continuous casting (for example belt casting or twin roll casting). DC casting produces a thick ingot that cools slowly during solidification. Continuous casting produces a thin, 3 - 20mm strip that cools quickly. The difference in cooling rate has a profound effect on the metallurgical structure of the cast product. These differences remain even after processing the ingot down to very thin gauge foil. By including DC casting, the process of the present invention produces a material that has properties comparable to those of continuous cast material. The control of the particle size of the DC cast material is important in obtaining these properties. In DC cast products, the cooling rate is

approximately 1 - 5°C per second depending on the ingot thickness. Finstock derived from the alloy should have high thermal conductivity after brazing (which typically occurs at 595°C to 605°C for times of about 2 - 10 minutes) combined with good strength (UTS) and corrosion potential. For ease of measurement, the thermal conductivity is usually implied by measuring the electrical conductivity. Both are reduced by elements in solution so there is a need to reduce the amount of soluble elements going into solution during brazing. This is achieved by controlling the particle size of the intermetallics and the dispersoids in the rolled sheet and the chemical composition of the sheet.

The high strength achieved by the DC cast material allows downgauging, to below 100µm, for example below 75µm, thus providing the ability to achieve new and improved lightweight fins. Additionally, the composition of the alloy has been chosen to maximise the absorption of brazing sheet scrap to ensure a low-cost production route, and maximise recyclability.

Preferably, the method further comprises the steps of heating or homogenising the DC cast ingot, hot rolling, cold rolling, and (inter)annealing, and may further comprise the step of cold rolling after the interannealing step. The final thickness reduction during cold rolling is preferably between 25 and 45%.

The homogenising step may be a two-stage homogenisation comprising heating the ingot to 580 - 620°C, holding for up to 8 hours, cooling to 460 - 500°C and holding for up to 8 hours.

Alternatively, the heating step may be a simple heat to roll step comprising heating to 460 - 540°C, and holding for up to 8 hours. This simple heat to roll step is not sufficient to bring about complete homogenisation of the ingot. It is intended to bring the ingot to a uniform temperature to facilitate hot rolling.

The hot rolling is preferably performed to 2.5 to 5.0mm, with an exit temperature from the hot mill of typically 280 - 360°C. Where an interannealing step is present, subsequent cold rolling to 50 - 700µm is

preferred. Cold rolling to final gauge without an intermediate anneal is followed by a final anneal.

The (inter)annealing step may be a single stage process at 250 - 450°C, preferably holding at this temperature for 2 to 4 hours. Alternatively, it may be a two-stage process comprising heating at 300 - 500°C (preferably holding for up to 4 hours) and subsequently cooling to 200 - 350°C (preferably holding for up to 4 hours).

Alternatively, annealing may be carried out in a continuous annealing furnace with the strip being fed through as a single strand to greatly increase the heating rates and reduce the holding times required. Higher annealing temperatures and shorter annealing times may thus be achieved.

The method may further comprise the step of brazing, wherein the particle size of the intermetallics and/or dispersoids present in the rolled product is sufficiently large such that the reduction in IACS is less than 5% units during brazing.

During the brazing cycle, small (sub-micron) dispersoids dissolve readily and increase the solute level. Rapid cooling after brazing retains substantially all of the solute in solution and this reduces the IACS value and the thermal conductivity. Increasing the mean dispersoid size reduces the amount dissolved during the brazing cycle and hence reduces the reduction in IACS and thermal conductivity. Dispersoid size is increased by using special homogenising and/or annealing treatments that coarsen the alpha Al(Fe, Mn)Si dispersoids and probably also coarsen some of the intermetallic particles. The homogenising treatment preferably comprises consecutive treatments at two temperatures, a first high temperature treatment followed by a lower temperature treatment. Annealing treatments may follow the same pattern.

In the absence of these special homogenising or annealing treatments, the dispersoids present in the sheet generally have a mean size substantially below one micron (as determined by the mean linear intercept method). The special homogenising and annealing treatments increase the mean dispersoids size, for example to greater than 0.5 microns preferably greater

than  $1\mu\text{m}$  and ideally greater than  $2\mu\text{m}$  but less than  $10\mu\text{m}$ . Thermodynamic calculations reveal that these particles are unlikely to transform during the brazing cycle.

The intermetallic particles (containing Fe Mn and Si together with other elements) are substantially larger than the dispersoids; their size is determined during solidification and possible break up during rolling.

According to a further aspect of the present invention, there is provided a method of producing an aluminium alloy finstock from an alloy comprising (in wt%):

Fe	0.8 - 1.5
Si	0.7 - 0.95
Mn	0.2 - 0.5
Zn	0.2 - 0.8
Mg	up to 0.2
Cu	up to 0.2
Ti	<0.1
B	<0.01
C	<0.01

Unavoidable impurities up to 0.05 each, 0.15 total

Al balance,

which method comprises DC casting the alloy, heating or homogenising, hot rolling, cold rolling, and annealing or interannealing.

The invention will now be described, by way of example, with reference to the following figures and examples, and in which:

Figure 1 is a flow diagram showing various processes of the present invention;

Figure 2 is a graph showing post-brazed strength trends;

Figure 3 is a graph showing corrosion potential trends (the left hand column of each pair relates to interannealed, and the right hand column relates to back annealed, i.e. annealed after cold rolling to final gauge);

Figure 4 is a graph showing post-brazed mechanical properties;

Figure 5 is a graph showing corrosion potentials; and



Figure 6 is a graph showing the relationship between post-brazed UTS and grain size.

Referring to Figure 1, there is shown various treatments of the DC ingot covered by the present invention, including the preferred conditions of each step.

### Example 1

Ingots approximately 1350mm x 600mm and weighing in excess of 7500kg were DC cast with the following composition:

Si	Fe	Mn	Cu	Mg	Zn	Ti	B
0.85	1.25	0.45	0.15	0.15	0.60	<0.05	<0.01

One ingot (route 1, Figure 1) was heated to 520°C and held for about 4 hrs before hot rolling to 3.0mm, with an exit temperature of approximately 325°C. The coil was then cold rolled to a transfer gauge of 400µm and then cold rolled to a gauge of 95µm, interannealed at 270°C for 2 hours at temperature, and further cold rolled to a final gauge of 63µm (final reduction of about 34%).

### Post-Brazed Properties:

UTS: 138MPa  
 % IACS: 46% IACS  
 Potential: -755mV (According To: ASTM G69 Standard Test Method For Measurement Of Corrosion Potentials Of Aluminium Alloys)

### Example 2

Material produced according to Example 1 as far as the transfer gauge (400µm) was taken and subjected to a range of interanneal temperatures between 200 and 400°C for about 2 hrs before cold rolling to 63µm gauge.

Post-brazed strength trends are shown in Figure 2 – interannealed route.

Corrosion potential trends are shown in Figure 3 – interannealed route.

Conductivity values are approx. 45% IACS.

Additionally, material at transfer gauge was cold rolled directly to 63µm and given a partial anneal (back anneal) at temperatures between 200 and 400°C.

Post-brazed strength trends are shown in Figure 2 – back annealed route.

Corrosion potential trends are shown in Figure 3 – back annealed route.

Conductivity values are approx. 45.5% IACS.

### Example 3

Material produced according to Example 1 as far as the transfer gauge (400µm) was taken and cold rolled to the following gauges:

253 µm, 125 µm, 95 µm and 89 µm

and interannealed (2 hrs at 270°C) before cold rolling to a final gauge of 63 µm. Final rolling reductions were:

>70%, 50%, 34% and 30% respectively.

Post-brazed mechanical properties are shown in Figure 4 (between 135-140MPa).

Corrosion potentials are shown in Figure 5 and are largely unaffected by interanneal gauge.

Conductivity is about 45% IACS.

Interanneal gauge is varied to maximise post-brazed grain size which benefits sag resistance during the braze cycle. For example, the thicker the interanneal gauge the smaller the grain size after brazing. Furthermore, the aspect ratio of the grains (length in the cold working direction to the thickness direction) increases as the interanneal gauge is reduced.

### Example 4

Material produced according to the composition noted in Example 1 was taken and heated to 460°C and held for approximately 4 hours before hot rolling to 3.0mm gauge. The coil was then cold rolled to a transfer gauge of

400 $\mu$ m and subsequently cold rolled and interannealed at 360°C, to a final gauge of 63 $\mu$ m. The final pass reductions were in the range 45 to 25%.

Figure 6 shows the relationship between post-brazed UTS and grain size.

To achieve maximum UTS the average grain size needs to be less than 50 $\mu$ m. However, reducing the post-brazed grain size does reduce the sag resistance of the material.

A balance between post-brazed grain size, UTS and sag resistance can be achieved by selecting specific combinations of:

- preheat temperature and soak time
- interannealing gauge
- final cold reduction.

CLAIMS

1. A DC cast alloy of composition (in wt%):

Fe	0.8 - 1.5
Si	0.7 - 0.95
Mn	0.2 - 0.5
Zn	0.2 - 0.8
Mg	up to 0.2
Cu	up to 0.2
Ti	< 0.1
B	< 0.01
C	< 0.01

Unavoidable impurities up to 0.05 each, 0.15 total  
Al balance.
2. An alloy of claim 1, wherein Cu is present in the range 0.05 - 0.2.
3. An alloy of claim 1 or 2, wherein Cu is present in the range 0.1 - 0.15.
4. An alloy according to any preceding claim, wherein Mg is present in the range 0.05 - 0.2.
5. An alloy according to any preceding claim, wherein Mg is present in the range 0.1 - 0.15.
6. An alloy according to any preceding claim, wherein Fe is present in the range 0.8 - 1.4.
7. A DC cast aluminium alloy finstock having a composition (in wt%):

Fe	0.8 - 1.5
Si	0.7 - 0.95
Mn	0.2 - 0.5

Zn 0.2 - 0.8

Mg up to 0.2

Cu up to 0.2

Ti < 0.1

B < 0.01

C < 0.01

Unavoidable impurities up to 0.05 each, 0.15 total

Al balance.

8. An aluminium alloy finstock according to claim 7, having a conductivity after brazing of at least 46% IACS.

9. A brazed heat exchanger having fins of the alloy of any one of claims 1 to 6.

10. A method of producing an ingot from an alloy of composition (in wt%):

Fe 0.8 - 1.5

Si 0.7 - 0.95

Mn 0.2 - 0.5

Zn 0.2 - 0.8

Mg up to 0.2

Cu up to 0.2

Ti < 0.1

B < 0.01

C < 0.01

Unavoidable impurities up to 0.05 each, 0.15 total

Al balance,

which method comprises DC casting the alloy to form an ingot.

11. A method according to claim 10, further comprising the steps of heating or homogenising the DC cast ingot, hot rolling, cold rolling, and annealing or interannealing.

12. A method according to claim 11, further comprising the step of cold rolling after the interannealing step.
13. A method according to claim 12, wherein the thickness reduction during the step of cold rolling after interannealing is between 25 and 45%.
14. A method according to any one of claims 11 to 13, wherein the homogenising step is a two-stage homogenisation comprising heating the ingot to 580-620°C, holding for up to 8 hours, cooling to 460 - 500°C and holding for up to 8 hours.
15. A method according to any one of claims 11 or 13, wherein the heating step comprises heating to 460 - 540°C and holding for up to 8 hours.
16. A method according to any one of claims 11 to 15, wherein the annealing or interannealing step is a single stage process comprising heating at 250 - 450°C.
17. A method according to any one of claims 11 to 15, wherein the annealing or interannealing step is a two-stage process comprising heating at 300 - 500°C and cooling to 200 - 350°C.
18. A method according to any one of claims 11 to 17, further comprising the step of brazing, wherein the particle size of the intermetallics and dispersoids present in the rolled product is sufficiently large such that the reduction in IACS is less than 5% units during brazing.
19. A method of producing an aluminium alloy finstock from an alloy comprising (in wt%):

Fe	0.8 - 1.5
Si	0.7 - 0.95

Mn 0.2 - 0.5

Zn 0.2 - 0.8

Mg up to 0.2

Cu up to 0.2

Ti < 0.1

B < 0.01

C < 0.01

Unavoidable impurities up to 0.05 each, 0.15 total

Al balance,

which method comprises DC casting the alloy, heating or homogenising, hot rolling, cold rolling and annealing or interannealing.

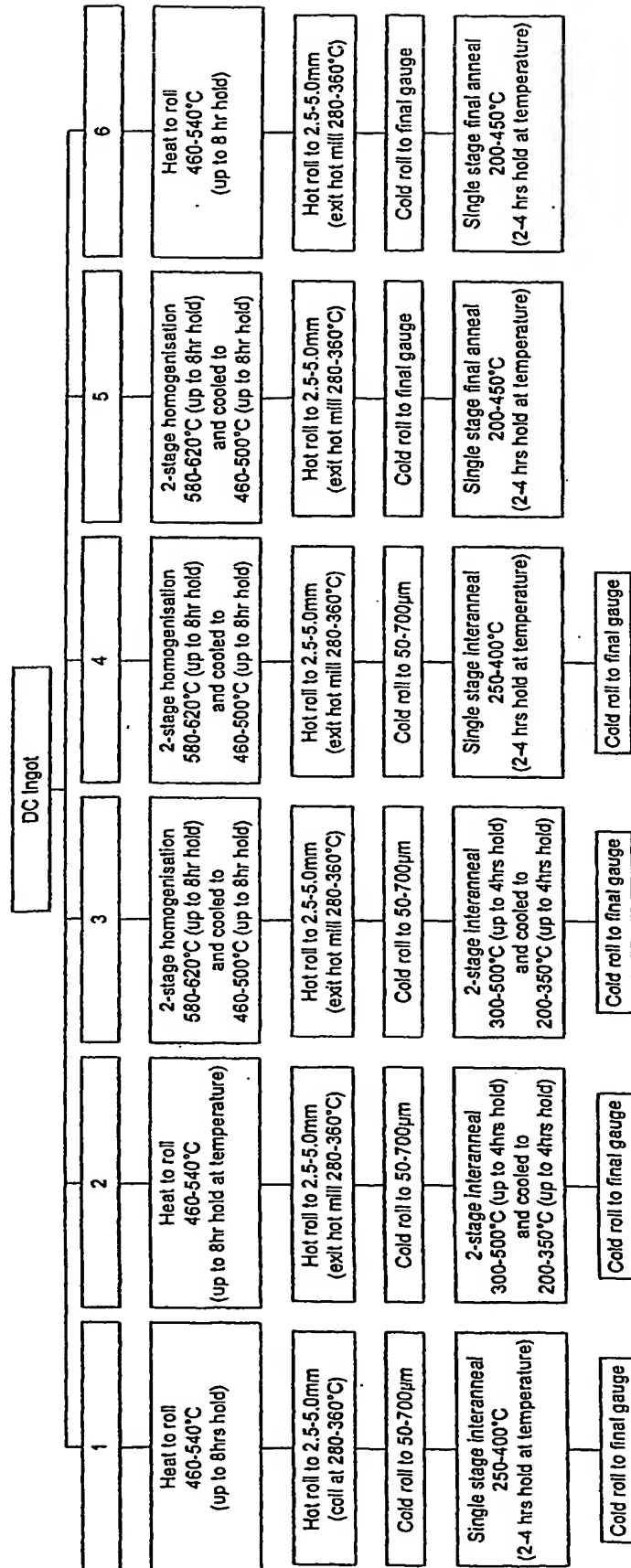


FIGURE 1



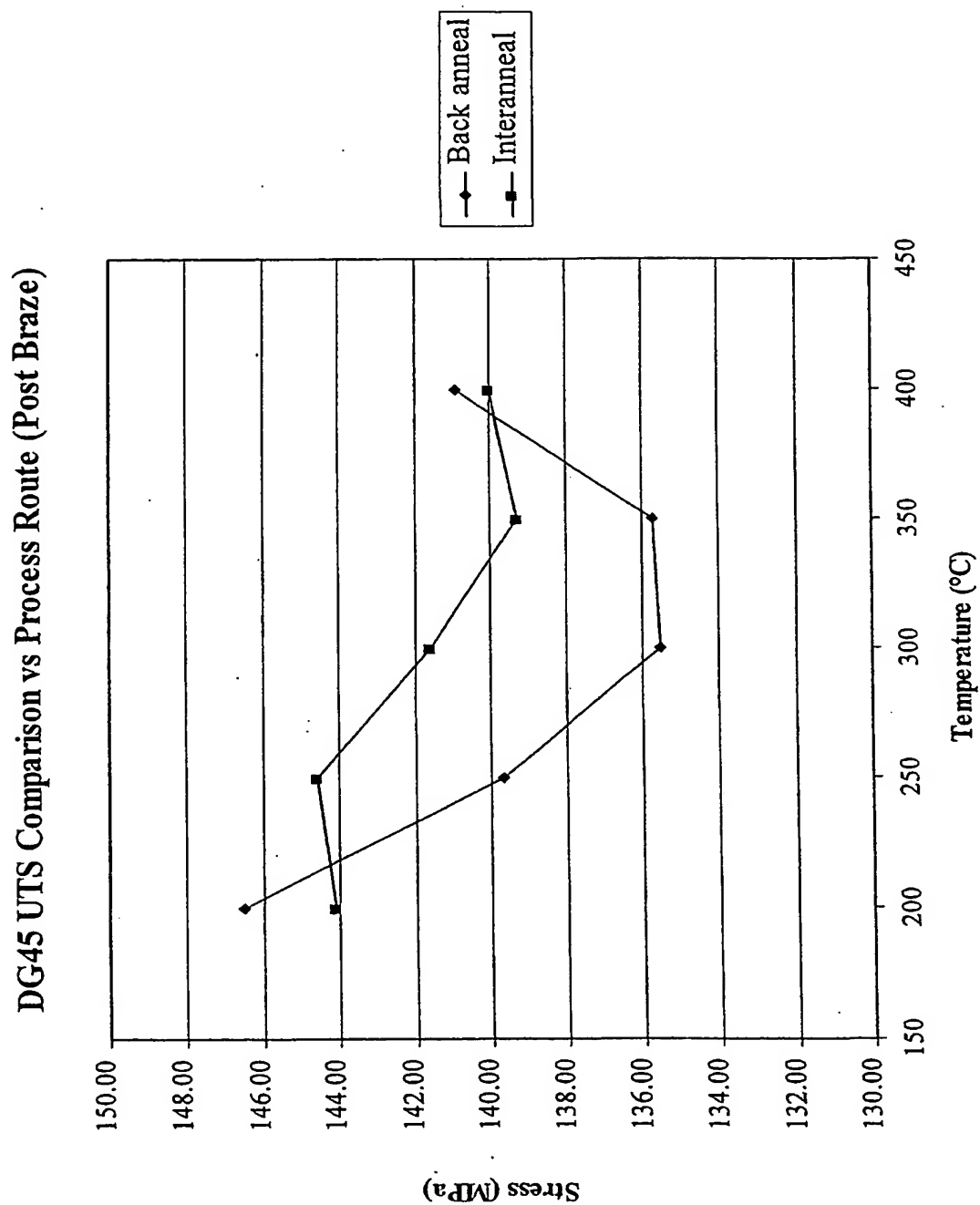


Figure 2

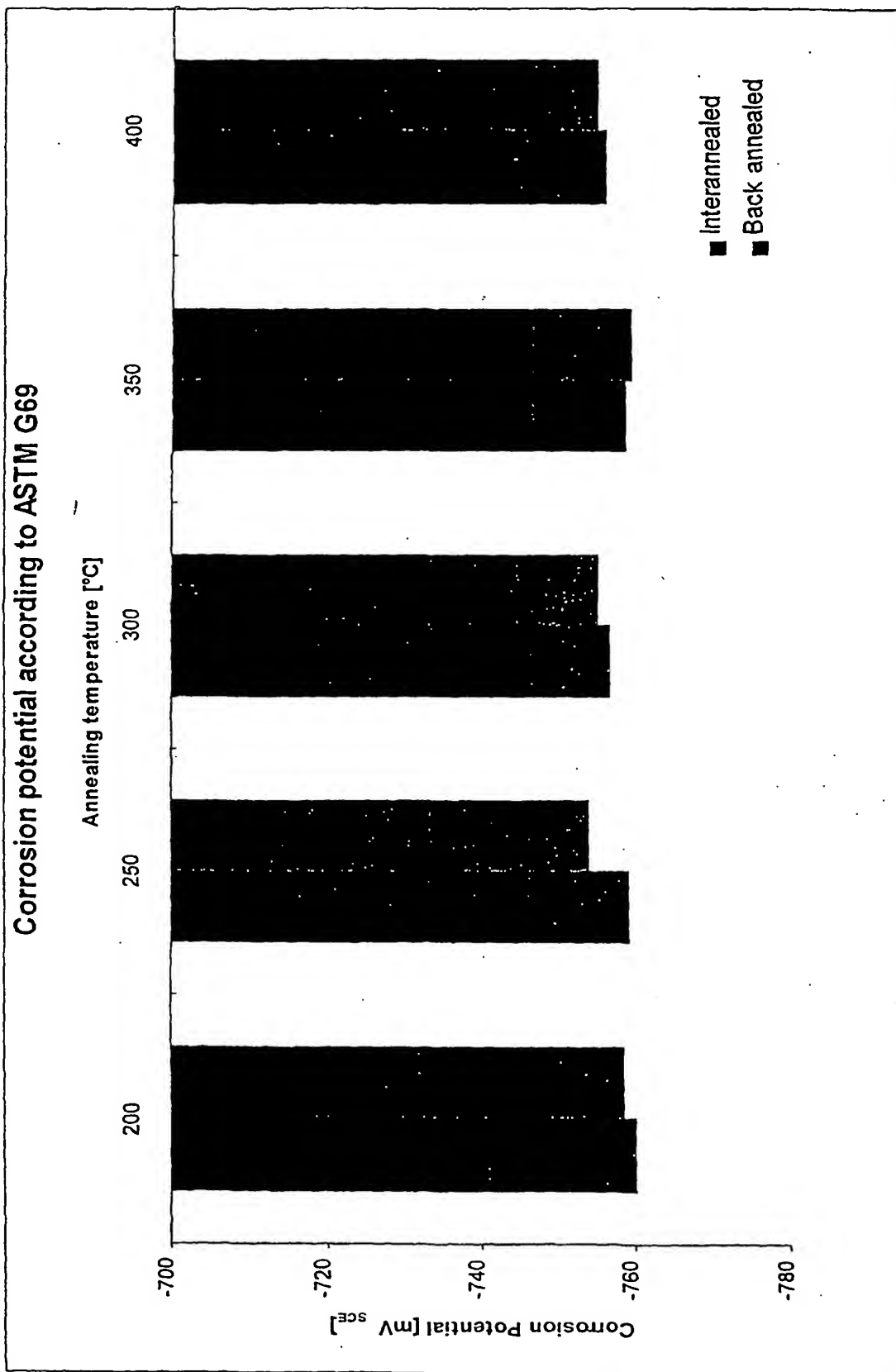


Figure 3

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UTS Comparison of Anneal Variants

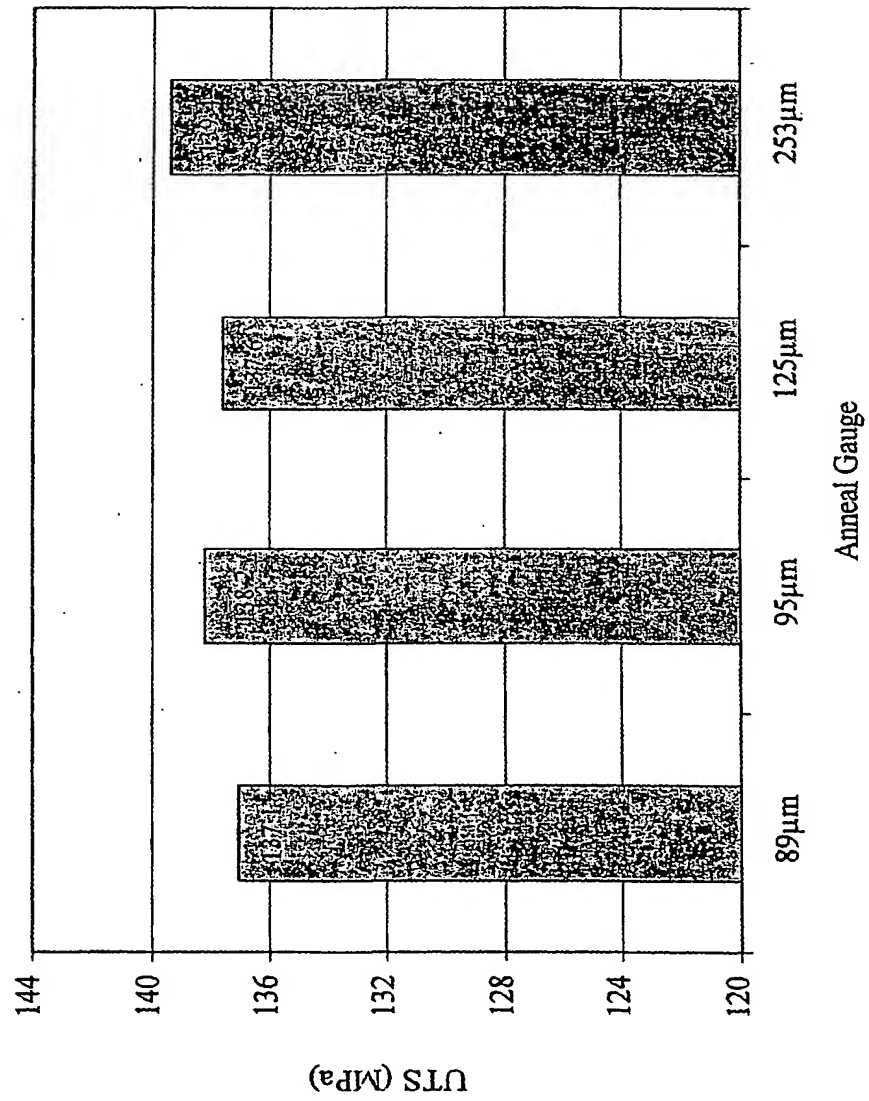


Figure 4

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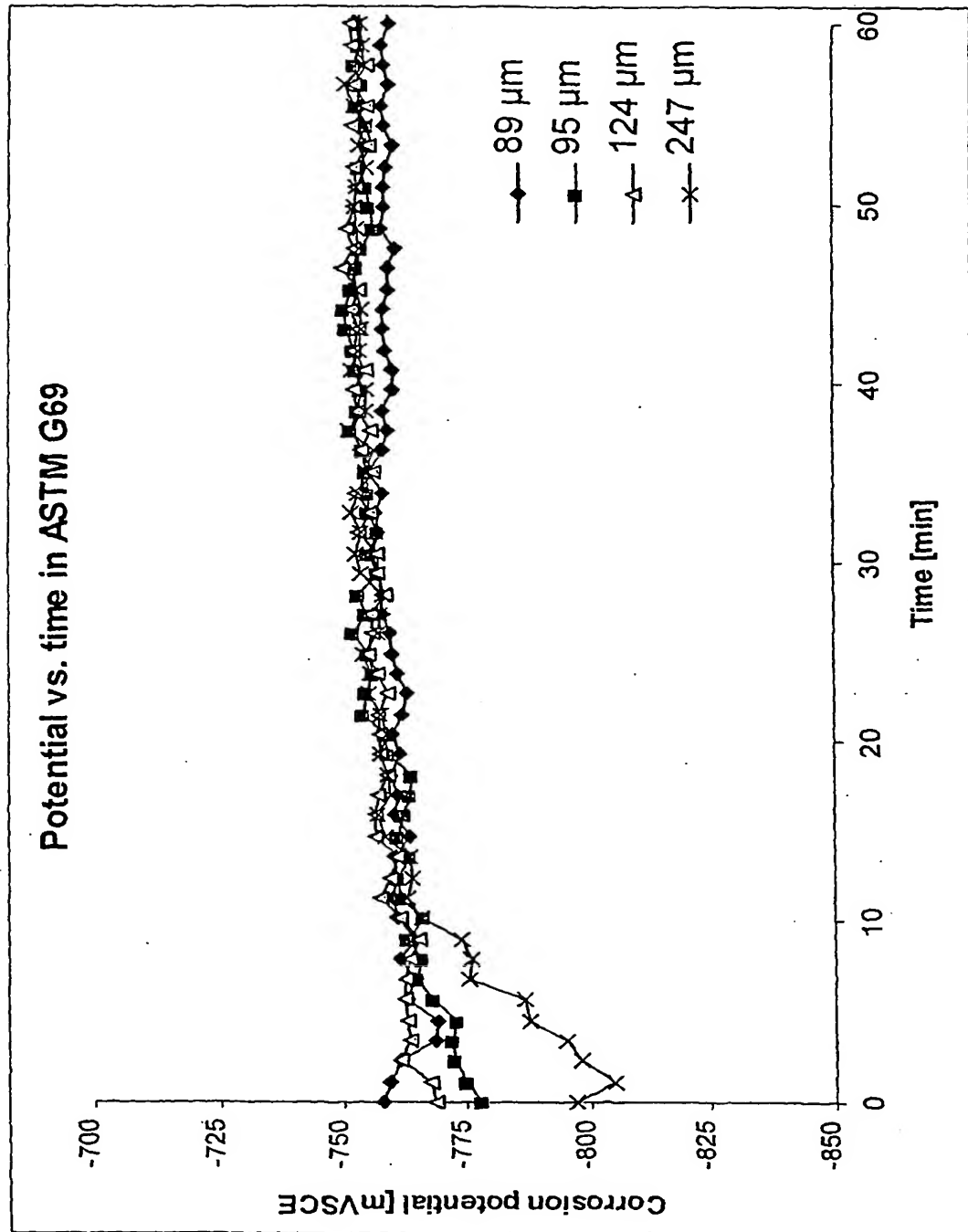


Figure 5

Avg. grain size / UTS relationship

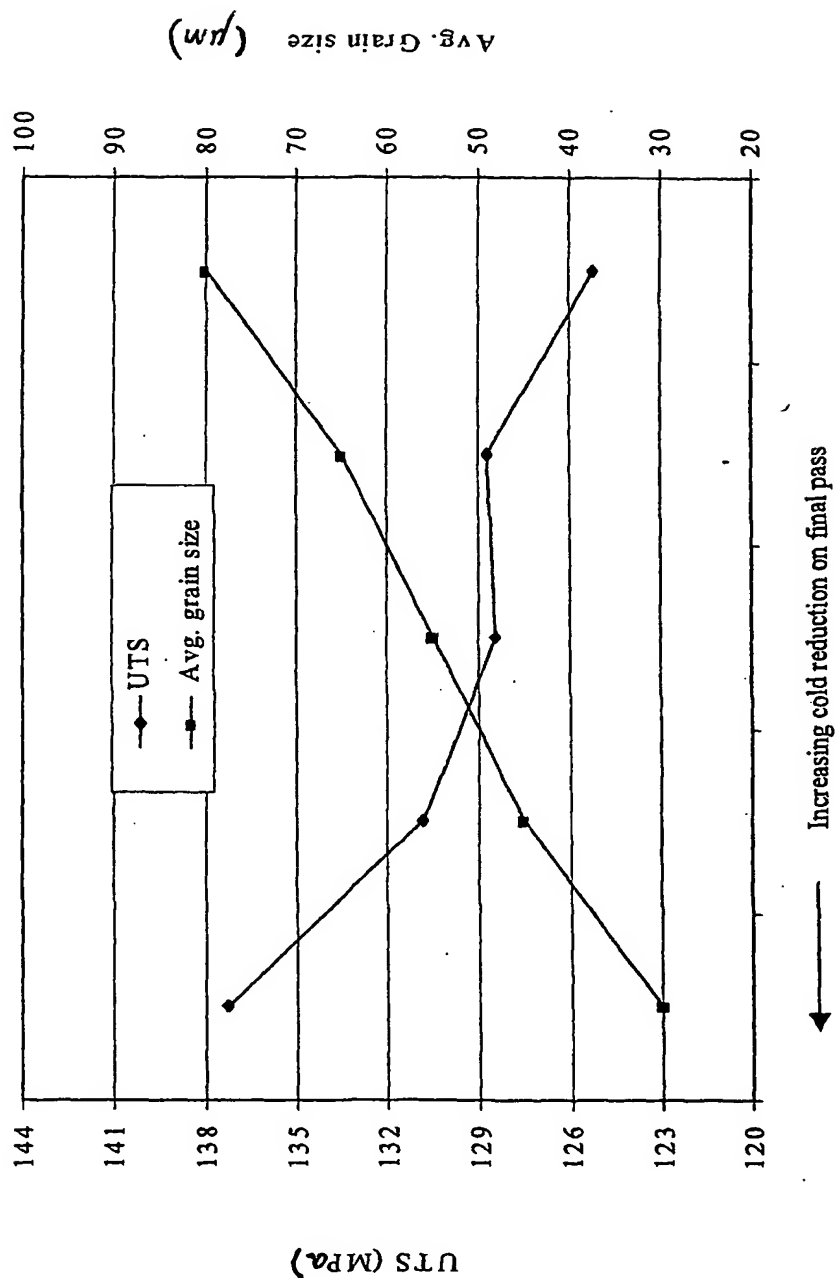


FIGURE 6

## INTERNATIONAL SEARCH REPORT

Intern Application No  
PCT/GB 02/01275A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C22C21/00 C22F1/04 //F28F21/08

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C22C C22F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00 05426 A (ALCAN INT LTD ;ANAMI TOSHIYA (CA); JIN ILJOON (CA); GALLERNEAULT W) 3 February 2000 (2000-02-03) cited in the application claim 1	1,6
P,X	WO 01 53553 A (ANAMI TOSHIYA ;GATENBY KEVIN (CA); JIN ILJOON (CA); ALCAN INTERNAT) 26 July 2001 (2001-07-26) claim 1	1,6

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

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Date of the actual completion of the international search

18 July 2002

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25/07/2002

Name and mailing address of the ISA

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## INTERNATIONAL SEARCH REPORT

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 0005426	A	03-02-2000	US 2001001402 A1	24-05-2001
			AU 5021899 A	14-02-2000
			BR 9912371 A	17-04-2001
			WO 0005426 A1	03-02-2000
			EP 1100975 A1	23-05-2001
			NO 20010361 A	21-03-2001
			US 6238497 B1	29-05-2001
			US 6165291 A	26-12-2000
WO 0153553	A	26-07-2001	US 6165291 A	26-12-2000
			AU 2822701 A	31-07-2001
			WO 0153553 A1	26-07-2001